AD-A218 215

REPORT DOCUMENTATION PAGE

	1b RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT Distribution unlimited
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Stanford University	5 MONITORING ORGANIZATION REPORT NUMBER(S) Office of Naval Research, N63374
6a NAME OF PERFORMING ORGANIZATION Stanford University	6b OFFICE SYMBOL (If applicable)
	7a NAME OF MONITORING ORGANIZATION Office of Naval Research, N63374
6c ADDRESS (City, State, and ZIP Code) Department of Chemistry Stanford University Stanford, California 94305-5080	7b ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, Virginia 22217-5000
8a NAME OF FUNDING SPONSORING ORGANIZATION Office of Naval Research	8b OFFICE SYMBOL (If applicable)
	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-86-K-0825
8c ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, Virginia 22217-5000	10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)
Picosecond Nonlinear Studies of Complex Materials Using the Free Electron Laser

12 PERSONAL AUTHOR(S)
Fayer, Michael David

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Final	FROM 86SEP15 TO 89MAR31	90Feb8	10

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

This project involves the use of the Stanford Free Electron Laser (FEL) to conduct picosecond optical nonlinear experiments to study complex materials. The theoretical foundation for the work has been established. A new four time correlation function approach for the analysis of optical nonlinear line narrowing experiments has been developed. The method explains previous experiments and will allow the FEL experiments to be analyzed to extract important dynamical information about complex materials. A full nonlinear optics laboratory has been established at the Stanford FEL. This includes necessary beam diagnostic equipment, optical components, computerized delay lines, liquid helium equipment, and detection equipment. The laboratory has the capability of performing photon echo and other nonlinear experiments.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION	
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS		
22a NAME OF RESPONSIBLE INDIVIDUAL Michael D. Fayer	22b TELEPHONE (Include Area Code) (415) 723-4446	22c OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

★ U.S. Government Printing Office: 1986—607-044

Final Report (Contract # N00014-86-K-0825)

Picosecond Nonlinear Studies of Complex Materials Using the Free Electron Laser

Michael D. Fayer
Department of Chemistry
Stanford University, Stanford, CA 94305

During this initial contract we made rapid progress in developing experimental capabilities at the Stanford Free Electron Laser and in developing a detailed theoretical description of a wide variety of ultrafast nonlinear experiments which are being employed in the study of complex solid state systems.

One of our most important accomplishments of this contract has been a series of theoretical developments which are revolutionizing the way optical experiments are used and interpreted in the investigation of solids with time evolving structures. In glasses, amorphous solids, complex crystals, proteins and other condensed matter systems, in addition to phonon induced fluctuations of local mechanical properties, there can be much slower timescale structural evolution.

The local structures associated with a glassy or amorphous system, such as an amorphous semiconductor, are not static even at very low temperatures (1.5 K). In glasses, small potential barriers separate different local mechanical configurations. Tunneling and thermal activation result in constantly changing local structures. This is in contrast to a simple crystal in which phonon induced fluctuations occur about a single equilibrium lattice structure.

Anderson and co-workers and Phillips independently proposed a model based on the Two-Level System (TLS) to describes structural

dynamics in glasses. TLS represent extra degrees of freedom characteristic of the glassy state. Briefly, a TLS is composed of two distinct local potential minima separated by a barrier. Changes in local glass structure are modeled as transitions between the two potential minima. There are a wide distribution of energy differences of the TLS potential minima and a wide distribution of tunneling parameters which are responsible for transitions between local configurations. Thus there is a very wide range of time scales associated with the dynamics of the TLS.

In addition to direct phonon induced fluctuations, the changes in the local configurations of a glass, amorphous solid, or crystal can modulate the electronic or vibrational state energies of a molecule or atom. If the molecules were not coupled to the environment, an absorption spectrum would reveal a line broadened only by the excited state lifetime (T_1). Since the chromophore is coupled to environment the energy levels fluctuate yielding a broader linewidth (frequency domain description) or alternatively a shorter dephasing time (time domain description). An absorption spectrum of a chromophore in a glass, amorphous solid, or a crystal will also be inhomogeneously broadened. Inhomogeneous broadening is a result of the wide variety of static local environments. To extract dynamical information from the dephasing of excited chromophores, it is necessary to obtain lineshape information with inhomogeneous broadening removed.

The state energies of chromophores in a complex solid will be influenced by processes in the medium which occur on a wide variety of time scales. The time scales will range from extremely fast fluctuations, to much slower configurational changes, and finally

totally static inhomogeneities. Because of the variety of time scales on which the medium affects the chromophore transition energies and therefore optical dephasing, it is necessary to carefully consider the sensitivity of various spectroscopic observables to the distribution of time scales.

Dephasing experiments have traditionally been treated with optical absorption formalisms. That is, the lineshape is related to the Fourier transform of a two-time transition dipole-moment correlation function. The optical absorption experiment is the Fourier transform of the optical free induction decay. It is sensitive to all time scales from the fastest fluctuations to the static inhomogeneities. In a solid, the inhomogeneous broadening will mask the dynamical information of interest. The two time correlation function is not an appropriate description for line narrowing experiments such as photon echoes, accumulated photon echoes, or hole burning experiments which are actually performed in chromophore-glass systems. We have recently developed an appropriate formulation for the interpretation of line narrowing experiments used to study complex systems. We have been able to derive and evaluate the correct four time correlation functions which properly describe the line narrowing experiments.

The photon echo experiment is a special case of line narrowing experiments describable by the four time correlation function. In the echo experiment, a pulse of light resonant with the optical transition of the chromophore excites the sample at time $t = 0$. A second pulse excites the sample at $t = \tau$. The echo, a coherent pulse of light, emerges from the sample at $t = 2\tau$. The intensity of the echo is measured as a function of the pulse separation, τ. The echo pulse

sequence removes static inhomogeneity *from the optical* dephasing measurement. It measures optical dephasing induced by random fluctuations on the timescale of τ.

Previously, optical line narrowing experiments applied to glasses and other complex materials have been described in terms of the two time dipole correlation function. We have proven that the correlation function which describes hole burning experiments, fluorescence line narrowing experiments, accumulated grating echo and incoherent photon echo experiments, and other line narrowing experiments, is the same as that which describes the stimulated photon echo. In fact the accumulated grating echoes, hole burning experiments, and the other experiments are completely analogous to the stimulated echo experiment. The stimulated echo is a three pulse sequence developed in magnetic resonance to measure spectral diffusion. There are <u>two</u> time scales in all of the optical line narrowing experiments except the photon echo. The first is τ, as in the echo experiment. The second is a much longer time, T_w. Optical experiments describable in terms of the stimulated echo four time correlation function will eliminate static inhomogeneous broadening, but will be sensitive to slow dynamics on the timescales out to the time T_w. For fluorescence line narrowing, T_w is on the order of the fluorescence lifetime. For accumulated grating echoes, T_w is on the order of the bottle neck state lifetime. In a whole burning experiment, T_w is on the time scale required to perform the experiment, i.e. write and read the hole. In a typical experiment, this is approximately 100 seconds. The photon echo experiment is the limit of all four time correlation function experiments in which T_w goes to zero. Therefore the echo experiment, in a system in which there exists a wide

distribution of time scales of dynamics, will yield the narrowest spectroscopic line. It is sensitive to only the fastest dynamics on the timescale of τ.

The important point is that each of the four time correlation function experiments is sensitive to dynamics on a different timescale. Since complex systems exhibit a wide distribution of time scales for dynamics and therefore optical dephasing, a combination of the echo experiment, which measures the homogeneous dephasing, and experiments such as the accumulated grating echo, in which T_w is not zero, which measure homogeneous dephasing and slower spectral diffusion processes, can provide a detailed picture of the multitime scale dynamics.

Our recent theoretical work now provides a detailed understanding of what the various experiments actually measure, and shows, contrary to popular belief, that these experiments are not equivalent. Of more importance is the fact that we now have a framework for going from the results of a combination of experiments to a detailed determination of underlying dynamics and solid state interactions. We have already been able to take data which has existed in the literature for years without explanation, and provide a complete description of the solid state dynamics which gives rise to the data. One of the main points to come from the theoretical investigations is that a combination of experiments, particularly the photon echo and the accumulated grating echo, can provide information that is impossible to obtain from a single experiment. To map out the complex dynamics in solids, which occur on a wide variety of time scales, it is necessary to do experiments on a variety of time scales. The photon echo provides the fastest time scale. The accumulated grating echo, by varying the duration of the

burst of pulses used, can provide information over a range of time scales slower than the echo experiment. The theoretical formalism shows that the results of such experiments are directly related to the LaPlace transform of the underlying distribution of the rates of the solid's dynamical processes.

The Stanford Free Electron Laser, with its ability to produce high intensity tunable picosecond pulses, is ideally suited to perform photon echo, accumulated grating echo, and transient grating experiments on broad classes of interesting materials. These include the electronic states of amorphous and layered semiconductors, vibrational states of molecules in solids, vibrational states of molecules absorbed on surfaces, and vibrational states of proteins, to name a few.

We have established a unique optical laboratory at the Stanford FEL to conduct photon echo, accumulated grating echo, and transient grating experiments. The echo experiments allow energy dynamics to be studied. The transient grating experiments permit direct investigation of transport phenomena, such as electron-hole diffusion in semiconductors.

We have now put into place a full experimental system for beam diagnostics, and computer controlled echo and grating experiments. The FEL is located in an underground tunnel some thirty feet below the optical laboratories. A beam transports system, which is low loss and achromatic, moves the beam up from the FEL into the optical laboratories. These labs were designed in conjunction with the group of Prof. Alan Schwettman, who is the director of the FEL. They provide the necessary environments for conducting sophisticated optical experiments.

For beam diagnostics, we have developed a modified version of a commercial autocorrelator for measuring pulse durations. The autocorrelator had to accommodate the macropulse structure produced by the FEL. We have the capability to measure the pulse duration at various times throughout the macropulse to determine if the pulse is evolving in its temporal characteristics. We have also developed a computer control gated integrator and monochromator system to examine the spectral characteristics of the laser pulses. The Stanford FEL produces an approximately 10 msec duration macropulse with the individual pulses separated by 85 nsec. We can examine the spectral characteristics individually of any of the pulses in the macropulse. We can step through the macropulse and determine if the pulse spectrum is evolving from the beginning to the end of the macropulse. We can also sit on one particular pulse in the macropulse and examine the shot to shot fluctuations in the spectrum.

In addition to the essential diagnostic equipment briefly described above, we have put into place a complete computer controlled photon echo, accumulated grating echo, and transient grating experimental system. The FEL beam emerges from the beam transport system which comes up from the tunnel where the FEL is located. It first goes through a system which allows a HeNe visible laser beam to be made to be precisely colinear with the FEL beam. This is used for the initial alignment procedures for setting up the complex nonlinear experiments. For the first experiments the FEL is running at 1.6 μm. The beam passes through a doubling crystal and the output, at 0.8 μm, is to conduct experiments on hydrogenated amorphous silicon in the band gap region. After doubling, the beam passes through an acousto-optic single

pulse selector. This is synced to the FEL pulses through a signal brought up from the FEL related to the accelerator RF. The pulse selector can pick out single pulses from the macropulse. In a typical experiment, every hundredth pulse will be selected from the macropulse. Thus many experimental measurements will be made during each macropulse. To do accumulated grating echo experiments, in which a string of pulses of variable pulse number is required, the pulse selector can be set to select any number of consecutive pulses from the macropulse.

Once a single pulse or pulse string has been selected it is directed into the optical set up to perform the nonlinear experiments. This consists of optical systems for making the appropriate pulse sequences, controlling intensities, aiming, focusing, and delaying the timing between pulses in the sequences. Polarizations are also controlled because experiments such as polarization gratings depend critically on the relative polarizations of the beams. A computer controlled dual delay line has been set up. This consists of a stepper motor delay stage for picosecond and subpicosecond time ranges. The stepper motor stage is on top of a long delay line and can be drawn along it, providing delays as long as 36 nsec. This dual delay line system permits the very short time behavior and the long time behavior of a sample to be examined without any change of optics or realignment of the optics. This is important for systems which exhibit dynamics over a broad distribution of time scales.

The sample can be placed either in a closed cycle refrigerator or in a liquid helium dewar to study the temperature dependence of dynamics and transport phenomena. The signal is detected by a photo diode or phototube and then sampled with a gated integrator. A second gated

integrator is used for normalization of the signal to the laser intensity. The outputs of the gated integrators go into a computer. Software has been developed to run the delay line and take data from the integrators in a manner that provides for multipass averaging and data manipulation. The system has graphics capabilities that permits the data to be viewed in real time as it is collected. The gated integrators can also be swept in time to measure fluorescence lifetimes from the samples. This is also computer controlled.

In summary, we have made important theoretical advances which will have a broad impact on the manner in which complex solid state systems are studied. We have put into place the experimental infrastructure necessary to conduct a variety of interesting and important experiments. The FEL system has undergone a number of successful development runs. We have brought the beam into the optical laboratories. The next series of FEL runs will produce useful experimental results.

This contract has been followed with the new contract, N00014-89-K0154. It is interesting to mention that during the initial phase of the new contract we have successfully performed detailed photon echo studies and have obtained initial accumulated echo data.

Publications from work supported by this contract

1. "Effects of Spectral Diffusion in Incoherent Photon Echo Experiments", Y. S Bai and M. D. Fayer, Phys. Rev. B, 37, 10440, (1988)

2. "Optical Dephasing in Glasses: Theoretical Comparison of the Incoherent Photon Echo, Accumulated Grating Echo, and Two Pulse Photon Echo", Y. S Bai and M. D. Fayer, Chem. Phys., 128, 135, (1988)

3. "Timescales and Optical Dephasing Experiments: Investigation of Dynamics in Complex Systems", Y. S Bai and M. D. Fayer, Phys. Rev, B. 39, 11066 (1989)

4. "A New Approach to the Nonlinear Spectroscopic Investigation of Dynamics in Complex Solids", Y. S Bai and M. D. Fayer, Comments on Condensed Matter Physics, 14, 343 (1989)